

Notes

Energy and Estrada index of phenylenes

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In the theory of polycyclic conjugated molecules, several remarkable results are known relating the properties of a phenylene with the analogous properties of a benzenoid molecule that in a natural way is associated with PH, called the hexagonal squeeze (HS) (for details see Fig. 1 or ref. 2). In the present work, the relationships between the energy, E , and the Estrada index, EE , of phenylenes and their hexagonal squeezes are examined. Within sets of isomers, a good linear correlation exists between E (phenylene) and E (hexagonal squeeze), as well as between EE (phenylene) and EE (hexagonal squeeze). The details of these correlations are established. Results show that an earlier obtained relationship between E (phenylene) and E (hexagonal squeeze) needs to be modified.

Phenylenes are polycyclic conjugated molecules, composed of four- and six-membered rings, such that every four-membered ring is adjacent to two six-membered rings, and no two six-membered rings are mutually adjacent. A great step forward in the theory of phenylenes was made by the discovery that many π -electron properties of a phenylene (PH) are closely related to the analogous properties of a benzenoid molecule, called its hexagonal squeeze (HS). The way in which HS is associated to PH should be evident from the examples depicted in Fig. 1.

What was first discovered (initially on a particular example¹, and then in the general case²) was that the algebraic structure count of a phenylene is equal to the number of Kekulé structures of the associated hexagonal squeeze; the fine details of this coincidence have been recently elaborated^{3,4}. Guided by this unexpected connection between the two classes of polycyclic conjugated molecules, several other relationships between PH and HS have been found, e. g., for the total π -electron energy^{5,6}, HOMO-LUMO separation⁶, Wiener index⁷⁻⁹ and its analogs¹⁰, Randić index¹¹, cyclic conjugation¹²⁻¹⁴, Narumi-Katayama index¹⁵, and PI index¹⁶. We report herein our findings on the analogous relations between energy and Estrada index.

Methodology

If $\lambda_1, \lambda_2, \dots, \lambda_n$ are the eigenvalues¹⁷ of G , a molecular graph, then its energy is defined as:

$$E = E(G) = \sum_{i=1}^n |\lambda_i|.$$

The graph energy is a quantity closely related to total π -electron energy (for details see refs¹⁷⁻²²). For some recent researches on graph energy, see earlier studies²³⁻²⁸ and the references cited therein. As explicated in the subsequent section, some earlier communicated results⁵ on the structure-dependence of E of phenylenes are now seen to require modification.

The Estrada index of the molecular graph, G , is defined as:

$$EE = EE(G) = \sum_{i=1}^n e^{\lambda_i}$$

This recently proposed²⁹ graph-spectrum-based molecular-structure-descriptor has already found a number of applications in biochemistry^{30,31}, quantum chemistry³², statistical thermodynamic³³, and elsewhere³⁴. We have recently undertaken a systematic study of the mathematical properties and structure-dependence of EE , embracing acyclic and benzenoid systems. The present work reports results on the structure-dependence of EE in the case of phenylenes.

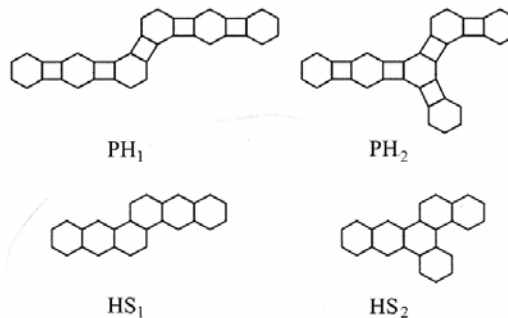


Fig. 1 — Two phenylenes (PH₁ and PH₂) and the corresponding hexagonal squeezes (HS₁ and HS₂). Both PH₁, PH₂, HS₁, and HS₂ have $h = 6$ hexagons. The phenylene PH₂ is branched, whereas PH₁ is unbranched.

Results and discussion

Relation between energy of phenylenes and their hexagonal squeezes

In the earlier study⁵, the following approximate relation between the energy of a phenylene PH and its hexagonal squeeze HS was obtained:

$$E(\text{PH}) \approx E(\text{HS}) + \sqrt{8}(h-1)$$

where h is the number of hexagons (in both PH and HS). This formula has two consequences:

- The expression $[E(\text{PH}) - E(\text{HS})]/(h-1)$ is nearly constant for all phenylenes, and is nearly equal to $\sqrt{8} \approx 2.83$.
- Within sets of isomers (for which h is constant), the correlation between $E(\text{PH})$ and $E(\text{HS})$ is linear. The regression lines have nearly constant slopes (independent of h), which are nearly equal to unity.

The property (a) was found to hold for a great variety of phenylenes, and no significant violation of it was observed⁵. On the other hand, the property (b) was not tested. We now establish that property (b) needs to be somewhat modified:

- Within sets of isomers, the correlation between $E(\text{PH})$ and $E(\text{HS})$ is linear. The regression lines have nearly constant slopes (independent of h), which are nearly equal to 0.5. Data points pertaining to differently branched PH/HS pairs lie on different and nearly parallel lines.

A characteristic correlation between $E(\text{PH})$ and $E(\text{HS})$ is shown in Fig. 2.

In view of the fact that the energies of differently branched phenylenes and hexagonal squeezes are correlated in a slightly different manner (see Fig. 2), we restricted our studies to unbranched species. For $h < 8$, the number of branched phenylenes is small and therefore the study of their correlations would not yield statistically reliable results. In Fig. 3, the correlation between the E -values of unbranched phenylenes with $h=7$ hexagons and of the corresponding hexagonal squeezes is shown. Data on the correlations between $E(\text{PH})$ and $E(\text{HS})$ for isomers with $h=4, 5, 6, 7, 8$ are given in Table 1.

From Table 1 we see that the slopes of the $E(\text{PH})/E(\text{HS})$ -correlations are, indeed, almost independent of the number h of hexagons, and that their values are very close to. On the other hand, the coefficient b depends on h , and this dependence is almost perfectly linear.

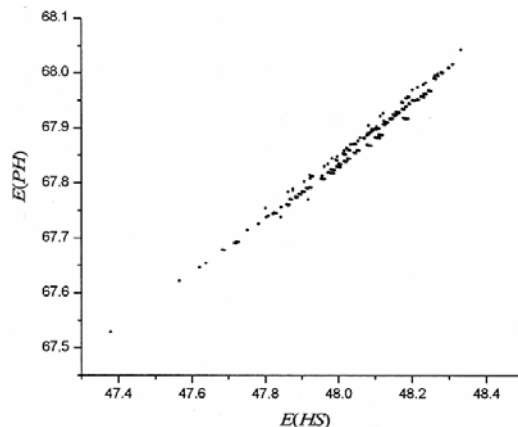


Fig. 2 — The energies $E(\text{PH})$ of 439 isomeric phenylenes with 8 hexagons plotted versus the energies $E(\text{HS})$ of the corresponding hexagonal squeezes. The data points form three almost parallel lines, corresponding to unbranched (190), singly-branched (207), and two-fold branched (41) PH/HS pairs. The corresponding regression lines are $E(\text{PH}) = (0.485 \pm 0.002) E(\text{HS}) + (44.6 \pm 0.1)$, $E(\text{PH}) = (0.483 \pm 0.002) E(\text{HS}) + (44.7 \pm 0.1)$, and $E(\text{PH}) = (0.480 \pm 0.006) E(\text{HS}) + (44.8 \pm 0.3)$, respectively, with correlation coefficients 0.9988, 0.9985 and 0.9969, respectively. The data-point in the upper right corner corresponds to the unique three-fold-branched PH/HS pair.

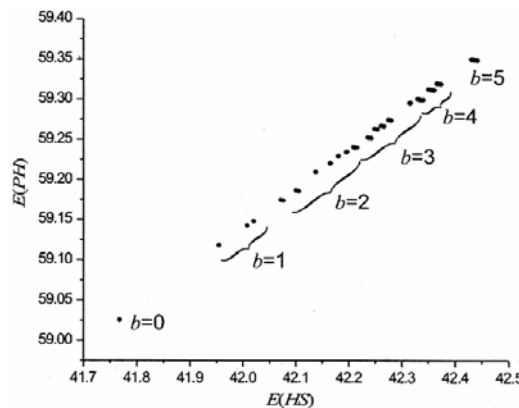


Fig. 3 — The energies $E(\text{PH})$ of 63 isomeric unbranched phenylenes with 7 hexagons versus the energies $E(\text{HS})$ of the corresponding hexagonal squeezes. For statistical data see Table 1. The data-points are grouped according to the number b of bay regions; for details see text.

From Fig. 3 we see that the number of data-points is apparently much smaller than the number of isomers considered. This happens because for some distinct PH/HS pairs, the data points almost completely overlap. A detailed examination revealed

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Table 1—Statistical data for the correlations of the form $E(\text{PH}) \approx aE(\text{HS}) + b$ for unbranched phenylenes (PH) and their hexagonal squeezes (HS) with h hexagons. N.I. = number of isomers, R = correlation coefficient.

h	N.I.	a	b	R
4	4	0.507 ± 0.008	20.9 ± 0.2	0.99975
5	10	0.497 ± 0.005	26.8 ± 0.2	0.99961
6	25	0.490 ± 0.004	32.8 ± 0.1	0.99942
7	69	0.486 ± 0.002	38.7 ± 0.1	0.99931
8	190	0.485 ± 0.002	44.6 ± 0.1	0.99880

that the grouping of the $E(\text{PH})/E(\text{HS})$ data points is based on the number b of bay regions, as indicated in Fig. 3.

The number of bay regions, b , was originally conceived within the theory of benzenoid molecules (for details see Fig. 4 and ref.³⁵). In the case of both benzenoid systems and phenylenes, this quantity is defined as¹¹

$$b = B + 2C + 3F + 4L$$

where B , C , F , and L are respectively the number of proper bays, coves, fjords, and lagoons on the perimeter of the considered molecule (Fig. 4).

In the examples given in Fig. 1, for PH_1 and HS_1 we have $B=2$, $C=F=L=0$, and therefore $b=2$, whereas for PH_2 and HS_2 , $B=2$, $C=1$, $F=L=0$, and therefore $b=4$.

In the theory of benzenoid molecules, it was established long time ago³⁶ that the two main factors causing energy differences between isomers are the number of Kekulé structures and the number of bay regions. In the case of phenylenes, instead of the Kekulé structure count one needs to consider the algebraic structure count. Since the algebraic structure count of a phenylene coincides with the Kekulé structure count of the corresponding hexagonal squeeze², it follows that the (only) main factor influencing the position of the $E(\text{PH})/E(\text{HS})$ data points should be the number b of bay regions. Our numerical studies fully corroborate this conclusion, which we formulate as:

- (d) Isomeric phenylenes with the same number of bay regions have nearly equal energies. The same holds for the hexagonal squeezes. Therefore, when $E(\text{PH})$ is plotted versus $E(\text{HS})$, the data points pertaining to species with equal h , but different b , form (almost) non-overlapping clusters.

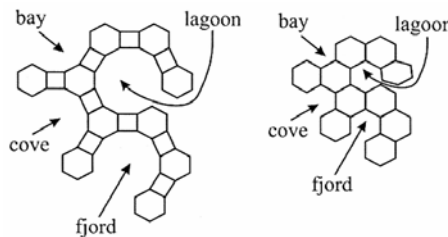


Fig. 4—Various features on the perimeter of a phenylene and its hexagonal squeeze, contributing to the number of bay regions (for details see text).

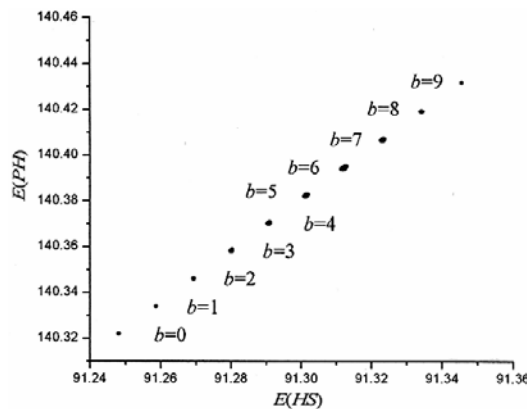


Fig. 5—The Estrada indices $EE(\text{PH})$ of the same phenylenes as in Fig. 2, versus the Estrada indices $EE(\text{HS})$ of the corresponding hexagonal squeezes. The data-points are grouped according to the number b of bay regions (for details see text). The statistical data for this correlation, as well as those for isomers with $h < 8$, are given in Table 2.

Relation between Estrada index of phenylenes and their hexagonal squeezes

We have studied the correlation between $EE(\text{PH})$ and $EE(\text{HS})$ for sets of isomeric phenylenes with $h=4, 5, 6, 7$, and 8 hexagons. The correlations are linear, and in contrast to what was observed in the case of energy (cf. Fig. 2), no separation between the data points pertaining to unbranched and branched phenylenes is observed. An illustrative example is given in Fig. 5. Bearing this in mind, we examined the $EE(\text{PH})/EE(\text{HS})$ -correlations for the sets consisting of all isomeric phenylenes (both unbranched and branched). The statistical data on these correlations are given in Table 2.

From Table 2 we see that in the case of the Estrada index also, the correlation is linear. In fact, the

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Table 2—Statistical data for the correlations of the form $EE(\text{PH}) \approx aEE(\text{HS}) + b$ for all isomeric phenylenes (PH) and their hexagonal squeezes (HS) with h hexagons. N.I. = number of isomers, R = correlation coefficient.

H	N.I.	a	b	R
4	5	1.137±0.006	14.6±0.3	0.999962
5	12	1.131±0.004	20.4±0.3	0.999932
6	37	1.128±0.002	26.2±0.2	0.999939
7	122	1.127±0.001	31.9±0.1	0.999934
8	439	1.125±0.001	37.7±0.1	0.999936

correlations found for the Estrada index are somewhat better than the analogous correlations for energy. As in the case of energy, the slopes of the regression lines are almost independent of the number h of hexagons, although their values are close to. The coefficient b varies with h in a linear manner.

Also, in the case of the Estrada index, the data points are grouped according to the number of bay regions. However, this grouping is much more exact than in the case of energy (see Fig. 5).

The Estrada indices of isomeric phenylenes with equal b values do not differ significantly. The same is true for the corresponding hexagonal squeezes. Yet, a closer examination of the relation between $EE(\text{PH})$ and $EE(\text{HS})$ for isomeric species with equal b , revealed some interesting peculiarities. This is illustrated in Fig. 6 for the case, $h=8$, and, $b=6$.

In Fig. 6, the $EE(\text{PH})/EE(\text{HS})$ data points are shown for the isomers with $h=8$ and $b=6$. As can be seen, the data points form three almost-horizontal lines. It was found that the bottom line pertains to unbranched, the middle line to singly-branched, and the top line to two-fold-branched phenylenes. This shows that the $EE(\text{PH})$ values depend on the number of branching hexagons of a phenylene, but are practically independent of the actual nature of the bay-type features. The $EE(\text{HS})$ values also depend slightly on the structure of the bay-type features: the data-points on the left hand ends of the horizontal lines correspond to phenylenes with maximal number of proper bays (B), whereas those on the right hand ends have minimal B values.

We summarize our findings on the correlation between the Estrada indices of phenylenes and their hexagonal squeezes in the following rules:

- (e) Within sets of isomers, the correlation between $EE(\text{PH})$ and $EE(\text{HS})$ is linear. The regression lines have nearly constant slopes (independent of h), which are nearly equal to 1.13. Data points

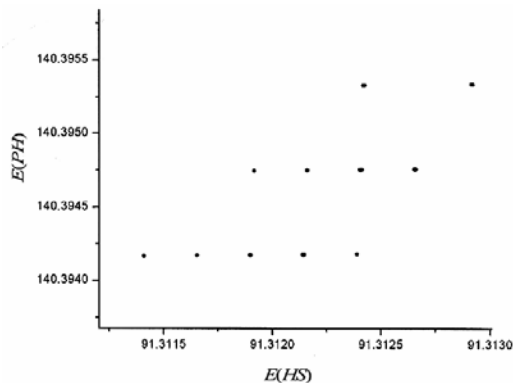


Fig. 6—The Estrada indices $EE(\text{PH})$ of the phenylenes with $h=8$ and $b=6$, plotted versus the Estrada indices $EE(\text{HS})$ of the corresponding hexagonal squeezes. Note that the number of bay regions is equal to 6 in the following cases: six proper bays ($B=6$), four proper bays and a cove ($B=4, C=1$), three proper bays and a fjord ($B=3, F=1$), two proper bays and two coves ($B=2, C=2$), two proper bays and a lagoon ($B=2, L=1$), a proper bay, a cove, and a fjord ($B=1, C=1, F=1$), three coves ($C=3$), a cove and a lagoon ($C=1, L=1$), and two fjords ($F=2$). Although all these 11 types of features occur at some of the isomers, the data-points appear to be smaller in number. This is because of the overlap of some data-points even at this very high resolution.

pertaining to differently branched PH/HS pairs lie on the same line.

- (f) Isomeric phenylenes with the same number of bay regions have nearly equal Estrada indices. The same holds for the hexagonal squeezes. Therefore, when $EE(\text{PH})$ is plotted versus $EE(\text{HS})$, the data-points pertaining to species with equal h and b almost perfectly overlap.

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